

Chapter Six

Conclusion

6.1. Overall Conclusion of Catalytic Performances

An intrinsically improved catalyst has been developed; even though proprietary catalysts have yet to achieve higher performance compared to their commercial counterparts. This is in view of the relatively good catalytic performance of the un-optimized catalysts which do not contain the harmful chromium-substance. Catalysts are uniquely nano-structured, the best batch have been prepared via the newer auto-ignition citrate-nitrate route. A total of 781 silica-supported solids have been prepared, comprising of a copper based compound in addition of a 2nd metal (M2 = Zn and Fe) and screened utilizing the 12 parallel high throughput hydrogenation reactors. All catalysts have been synthesized and performances validated at an elevated time. The identification of lead catalysts as demonstrated were facilitate by the aids of the screening campaigns; the practical reduced (in quantity) of the final materials for the time-consuming characterization were achievable by strategic rational approach and chemical intuition as emphasized in the Combinatorial Philosophy.

For the liquid hydrogenolysis of methyl laurate, testing time have been reduced in great length; in which by reality would not be near achievable using conventional single autoclave unit. The exploration and identification of catalyst 'leads' are carried out in a control and systematic way, the best catalysts being channeled into characterization loops for various analytical techniques.

Of all previously mentioned, 28 catalysts were carefully chosen and reported in this work. From the results, catalysts prepared from metal citrate-nitrate compounds supported on silica exhibited a high activity and selectivity compared with conventional catalysts prepared with metal nitrate compound. Specifically, the catalyst 'leads' could be identified as the top-ranked B14 of the binary Cu-Zn at at/at 3:1, seconded by B11 of the binary Cu-Fe at at/at 3:1. The fact that these catalysts are prepared from DIWI indicated that the role that the active metal loading (especially copper) played is of secondary importance after the influence of precursor. In addition, it can be concluded that the addition of a 2nd metal, Fe or Zn especially, has been successfully implemented to the mono-metallic Cu catalysts system, with an improvement of overall catalyst activity observed especially for the binary metal system at at/at ratio 3:1. The mono-metal zinc or iron has not shown any catalytic activity at the same reaction condition. This has led to the supposition of the effectiveness of copper metal in catalyzing this reaction, and the addition of a 2nd metal (zinc or iron) is attributed to a real promoting effect.

On this basis, 10 catalysts from the Cu-Zn and Cu-Fe have been screened and channeled into the characterization techniques. As normal, the highest catalytic materials have been chosen. However, for better comparison and understanding, several inactive catalysts at comparable composition and synthesis method are also chosen in addition to the two performed catalysts, i.e., B14 and B11. The information generated from characterization has revealed the molecular aspects of catalyst preparation, the role of the support and the different interactions taking place between the metal complex and support. The postulation feedback has been necessary to assist the next phase of work to be carried out with sample materials.

6.2 Overall Conclusion of Catalyst Properties

The characterisation was important to substantiate the structural extrapolations gained from the high throughput testing described in chapter 4. The variance in the parameter field of the ten studied catalysts is too large to allow for a single quantitative multivariate regression analysis of the catalytic performance with the characterisation data. Several models tried gave no statistically relevant correlation coefficients.

The characterisation data allow, however, to renormalize the observed catalytic activity data and thus to draw some conclusions for further synthesis campaigns. The essential data are collected in Table 6.1

Table 6.1: Summary of characteristic parameters of the catalyst families studied. Colours denote the synthesis parameters (yellow: P1, red: P2 Cu-Zn series, blue: P2 Cu-Fe series).

1	2	3	4	5	6	7	8
Catalyst	TPR Cu (%)	Cu loading at %	Available Cu at %	Catalytic activity mmol/g/h	Specific activity per at % Cu	BET surface area (m ² /g)	Specific activity per m ² and Cu
B08	96	10	7	37	5.3	391	1.3
B14	88	7	6	78	13	286	4.5
B12	100	5	5	24	4.8	158	3.0
B13	100	2	2	26	13	174	7.4
B07	88	12	10	3	0.3	190	0.1
B01	81	17	14	3	0.2	21	0.9
B11	68	6	4	50	13	235	5.5
B09	41	4	2	25	13	230	3.9
B10	37	2	1	33	33	304	10.0
B04	58	10	6	8	1.5	213	6.0

Column 5 reports the observed catalytic activities per unit mass of catalyst. Such data allow selection of the best catalyst from a series of given samples but are not very informative in finding the correlations between function and preparation parameters. It becomes immediately obvious that the activity does not scale either with the absolute

Cu loading (col. 3) or with the reducibility (col. 2). An almost inverse correlation is obtained when the activity is considered as function of the available Cu content (col. 4) which is the normalised value from col. 2 and 3. This indicates that dispersion does matter and that loadings above some 5 at% of Cu that is reducible are detrimental for the activity. The next expectation would be that the activity scales with the surface area of the catalyst, which would be reasonable if the dispersion of Cu would not change with the reduction of surface area from the value of the bare support. Comparison of col. 5 and 7 quickly show that this is also not the case and that the Cu species present do change with the synthesis protocol. From this finding it is clear that catalysts from different synthesis routes may not be compared for their specific activity and that it is not obvious which route has the highest catalytic potential.

An interesting analysis of the specific activity of various types of Cu particles obtained is possible when the activity is normalised with respect to the available Cu abundance (col. 5 and 4 to yield col. 6). First, it is noted that the specific activity of Cu can vary over two orders of magnitude. Second, it is strongly emphasized that overloading drastically reduces the specific activity. More surprising is the fact that no principal distinction between Zn and iron as more effective structural promoter is possible. The highest specific activity is observed in the Cu-Fe family. The value allows conclusion that a substantial increase in effectiveness of the system is still possible if synthesis conditions were chosen to combine the specific activity of B10 with the loading of active sites of B14. For this synthetic target the following handles are available:

- Avoid hydrolysis of the citrate complexes.
- Avoid overloading with active Cu.
- Optimize calcination temperature.

- Take care that no excess nitrate can form a mesophase prior to the explosion reaction with citrate.
- Increase the strength of interaction of Cu with the M2 component by using even less reducible elements that react with silica such as zirconia or ceria.
- Use hydrogen donors such as noble metal additives or zirconia to circumvent transport limitations by incomplete phase mixing of hydrogen with the liquid phase.
- Maximize the abundance of Cu vs. the loading with M2 to get a maximum coverage of Cu particles without blocking all mesoporous structure and hence blocking the transport pathways to the active phase.
- Test for such transport limitations in a better reaction environment such as in a trickle flow reactor.

It is also seen that the synthesis method of P1 is not good, as it does not lead to a sizeable abundance of active Cu. The postulated synergistic effect of the M2 element is obvious from the data but it can also be seen that the presence of the M2 element alone is not sufficient as either no effect or even detrimental influences are manifest as well as the beneficial effects.

It should also be possible to correlate the performances of the catalysts to the surface area exposed. If small Cu particles are important then the surface area per unit mass should scale with the catalytic performance. The relevant normalisation is given in col. 7 of table 6.1 and shows again that there is a huge variation in these data. This in itself shows that other factors not quantified with the parameters given in the table play an important role. The most obvious missing factor is the size and shape distribution of the active Cu particles that will require in-situ TEM analysis for its determination.

The data reveal that Fe is the most effective modifying element but that it was not suitably optimised in terms of site density. The lacking of control over the texture during drying of the citrate-nitrate precursors is the most relevant step to be improved. A modification of the pH and a change in drying time (e.g., increase of velocity by spray drying) are the practical handles for optimisation. The principal better effect of Fe over Zn supports the notion that stronger fixing support oxides should be tested. In the catalyst design care must be taken to avoid surface acidity development that may interfere with the organic chemistry and give rise to deactivation by coking. Fe and Zn are amphoteric and thus essentially neutral in carbon-carbon bond chemistry. The reaction of zirconia or ceria with silica will remove excess acidity and/or modifiers such as Li or atomically dissolved Cu will quench the surface acidity of thicker layers of the strongly bound support oxides. Finally, thermal treatment may remove most Brönsted acidity so that a multitude of options are available to control the surface acidity of the suggested new catalyst formulations.

The data in col. 7 further imply that even in the present systems there is still a huge potential for improvement of performance as the “good” catalysts B14 and B11 are only half as effective in their specific activity (Col. 8) as the samples (B13, B10) with the most active Cu particles.

In conclusion the characterisation of two families of samples has given full support to the optimistic conclusions from the high throughput testing that a replacement of the technical Cr-containing systems with the eco-friendly Cu-M2 systems is well conceivable. Future optimisations should concentrate on the Cu-Fe system, augmenting the fixing effect of M2 by co-addition of ceria or zirconia and by ensuring that hydrogen dissociation and surface abundance of active hydrogen are not rate-limiting.

This can be achieved by promotion with a group VIII element and/or by intensifying the gas-liquid transport in going from slurry phase reactors to trickle flow systems.

With respect to the methodology of characterisation, it was shown that a combination of TPR with BET and SEM-EDX is a very powerful strategy that can be applied to a large number of samples and as such create a data set similar to that in Table 6.1 with sufficient resolution of parameter space to allow for a regression analysis. Thus enables the predictability of the relevance of key influence factors of the catalyst material on performance. In future, the details of the synthesis protocols such as pH of treatment, concentration of complexing agent, calcination conditions and reactivity of support with the M2 additive should be pre-determined in dedicated experiments (titration) to ensure that the reactions occur between the expected species and not between species precipitating from solution with a chemical constitution different from the what is intended. The thermochemistry likewise requires more optimisation to avoid unnecessary sintering of CuO particles as it is unfavourable to choose the maximum synthesis temperature far above the operation temperature of the system.

It is apparent that the practiced combination of high throughput screening with selective high-level characterisation is a very powerful strategy to improve the performance of a given catalyst system based on a firm understanding of the critical parameters of the system.

6.3. Future Prospects and Challenges

As speed and efficiency in the discovery of new material application and processes drive almost everything in industry today, much effort has been devoted to accelerate the discovery of new materials and processes. Combinatorial Technology is the most successful approach and as such, this is where COMBICAT and dedicated team work are focused intensively on.

Combinatorial Technology has become an accepted practice in pharmaceutical drug discovery. Since then heterogeneous catalysis has emerged as one of the most promising areas for utilization of this methodology, gaining much recognition in the last decades. The high throughput experimentation and catalyst screening with the approach of combinatorial chemistry enables researchers to accelerate fruitful scientific findings from a wide space of probability. Positive clarification on the initial skepticism with respect to the possibility of obtaining meaningful catalytic data aided by rational approach and data analysis (underlines in the Combinatorial Philosophy) has subsequently lead to substantial investments by many chemical companies into the high throughput experimentation [Dagani R., 2002].

COMBICAT Research Centre has applied such an approach in the development of catalyst for the production of fatty alcohol from hydrogenation process of fatty acid methyl ester by using 12 parallel High Throughput High Pressure Reactor. The focus of such utilization at the present phase is on the optimal catalytic performances of proprietary catalyst in the hydrogenolysis reaction.

In view of this, severe de-bottlenecking of suitable informatic data analysis, storage, data retrieval, data mining and library design were continuous undertaken. Fundamental understanding of catalytic reactions and its catalyst properties have been demonstrated to be greatly beneficial. Thus the continuous successes of project requires extreme teamwork of researchers, chemical engineers and software engineers; not to forget also sophisticated and ideally in-situ characterization equipments.

Finally, the acceleration technique by high throughput tools in addition of firm fundamental understanding of catalyst through various characterizations is indeed powerful as demonstrated, thus bridging the gaps of Industrialist and Academia demands. Such could only be realized by the close embracement of Combinatorial Technology and its applications.